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ARS 51-26
August 1968

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Biphenyl Residues in Oranges:

Effect of Biphenyl Dosage and Pad Placement

Shirley Norman, G. L. Rygg, and D. C. Fouse,
Agricultural Research Service, U.S. Department of Agriculture

SUMMARY

Biphenyl residues in oranges were higher and fruit decay was lower in cartons with the pads placed between fruit layers than in cartons with the pads at the top and bottom.

Oranges in nonvented cartons absorbed more biphenyl than oranges in vented cartons.

Biphenyl residues in oranges increased as the number of pads per carton increased regardless of the biphenyl dosage.

Biphenyl absorption increased with waxing and with number of coats of wax.

Biphenyl residues in oranges apparently cannot be decreased significantly by regulating the dosage per carton with the present commercial formulation.

INTRODUCTION

Biphenyl has been used for control of spoilage in citrus fruit since Tomkins first reported its effectiveness in 1935 (7). The legal tolerance for biphenyl residues in citrus fruits in the United States has been 110 p.p.m. since 1956 (3, 4). Recently a legal tolerance of 70 p.p.m. (effective July 1, 1968) was adopted by the European Economic Community (EEC) (2). To insure that an adequate quantity of biphenyl is available during the marketing period, whether domestic or overseas, the commercial practice is to use kraft paper impregnated with biphenyl at the rate of 4 to 5 pounds per thousand square feet of paper. Two sheets (pads) are placed in each carton of citrus fruit during packaging; pad placement varies with individual packinghouses. Previous work[1] indicated that oranges might exceed the EEC tolerance of 70 p.p.m. with the prolonged storage required for overseas shipments. Preliminary studies were undertaken to determine to what extent biphenyl residue levels could be controlled by regulating the amount of biphenyl and the position of the pads. Studies were also made of the effect of wax coatings on the absorption of biphenyl by navel oranges.

EXPERIMENTAL METHODS

Fruit.--Navel oranges furnished by Sunkist Growers Inc., Ontario, Calif., were washed and waxed by standard packinghouse treatments except where wax coatings were compared. Size 138, consisting of five layers of fruit per carton, was chosen for this work. Oranges used for wax comparisons were waxed by the Sunkist Growers' Field Research Department. The oranges were brought to storage temperature, repacked in standard cartons with biphenyl pads placed in appropriate positions, and then placed in storage.

Biphenyl pads.--Crown Zellerbach Corp., San Francisco, Calif., furnished pads with different levels of biphenyl. The levels of biphenyl applied to the pads were:

(1) 5.13 lb. per 1,000 sq. ft. (2.41 g. per pad by analysis);

(2) 2.93 lb. per 1,000 sq. ft. (1.40 g. per pad by analysis);

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[1] Rygg, G. L. Biphenyl content, transit temperature, and fruit condition of California citrus in overseas shipment. U.S. Dept. Agr. (In preparation.)

(3) 1.88 lb. per 1,000 sq. ft. (1.07 g. per pad by analysis);

(4) 1.17 lb. per 1,000 sq. ft. (0.55 g. per pad by analysis).

Each pad was sampled for analysis by punching out several 1/4-inch disks before and after use.

Fillers.--Standard biphenyl pads were aired until all the biphenyl had volatilized from the pads. The pads retained the mineral oil and parrafin wax used in formulation.

Fruit sampling.--After the required storage, the fruits were examined for decay and soilage and 20 oranges were selected by random numbers (1, pp. 299-300) for biphenyl analyses.

Series A.--Triplicate vented cartons of fruit (1) without biphenyl pads, (2) with standard biphenyl pads (2.32 g. per pad) placed at the top and bottom, and (3) with pads placed between the first and second and the fourth and fifth layers were compared. Storage periods and temperatures were:

(1) 4 weeks at 42° F.;
(2) 4 weeks at 42° plus 1 week at 70°;
(3) 4 weeks at 42° plus 2 weeks at 70°;
(4) 4 weeks at 50°;
(5) 4 weeks at 50° plus 1 week at 70°;
(6) 4 weeks at 50° plus 2 weeks at 70°.

Series B.--Biphenyl residues associated with pad placement, biphenyl dosage, and vented and nonvented cartons were compared during 4 weeks' storage at 50° F. Duplicate cartons were sampled at 1- and 2-week intervals. Pad placements, biphenyl dosages, and carton venting were:

(1) Two pads (2.32 g. biphenyl per pad) per carton were placed at the top and bottom and between the first and second and the fourth and fifth layers in vented cartons. Cartons with pads between layers were considered the controls for the entire series.

(2) Two pads (1.40 g. biphenyl per pad) per carton were placed at the top and bottom and between the first and second and the fourth and fifth layers in both vented and nonvented cartons.

(3) Three pads (1.07 g. biphenyl per pad) per carton were placed between the second and third, the third and fourth, and the fourth and fifth layers in both vented and nonvented cartons.

(4) Five pads (0.55 g. biphenyl per pad) per carton were placed under each layer in both vented and nonvented cartons.

(5) Three pads (0.55 g. biphenyl per pad) per carton were placed between the second and third, the third and fourth, and the fourth and fifth layers in both vented and nonvented cartons.

Series C.--Biphenyl residue levels from triplicate cartons of oranges stored in vented cartons with standard biphenyl pads were compared to those stored with kraft paper fillers between the biphenyl pad and the oranges. Biphenyl dosages and pad placements were:

(1) Two pads (2.32 g. biphenyl per pad) per carton were placed at the top and bottom of the cartons with and without fillers.

(2) One pad (2.41 g. biphenyl per pad) was placed between the third and fourth layers with and without fillers.

Series D.--Biphenyl residues in fruit in single cartons of nonwaxed fruit and fruit waxed with one, two, and three coats of five different waxes were compared. Standard biphenyl pads (2.32 g. per pad) were placed between the first and second and the fourth and fifth layers of fruit. All the fruit was stored 4 weeks at 50° F. in cartons vented with 18 1-inch holes per carton.

Biphenyl residues.--Twenty fruits from each carton and 0.1 to 1.0 g. from biphenyl pads were sampled and biphenyl residues determined by thin layer chromatography and spectrophotometric measurements according to Norman and coworkers (5). Results for fruit were calculated as p.p.m. of biphenyl on the basis of whole fresh fruit weight and as grams per carton on the basis of 18 kg. of fruit per carton. Results for pads were calculated as grams per pad and grams per carton.

RESULTS AND DISCUSSION

Average biphenyl residue levels from series A are shown in figure 1. Oranges stored 4 weeks at 50° F. absorbed more biphenyl than those stored at 42°, and oranges in cartons with pads between layers absorbed more biphenyl than those in cartons with pads at the top and bottom. Biphenyl content in oranges after additional storage of 1 and 2 weeks at

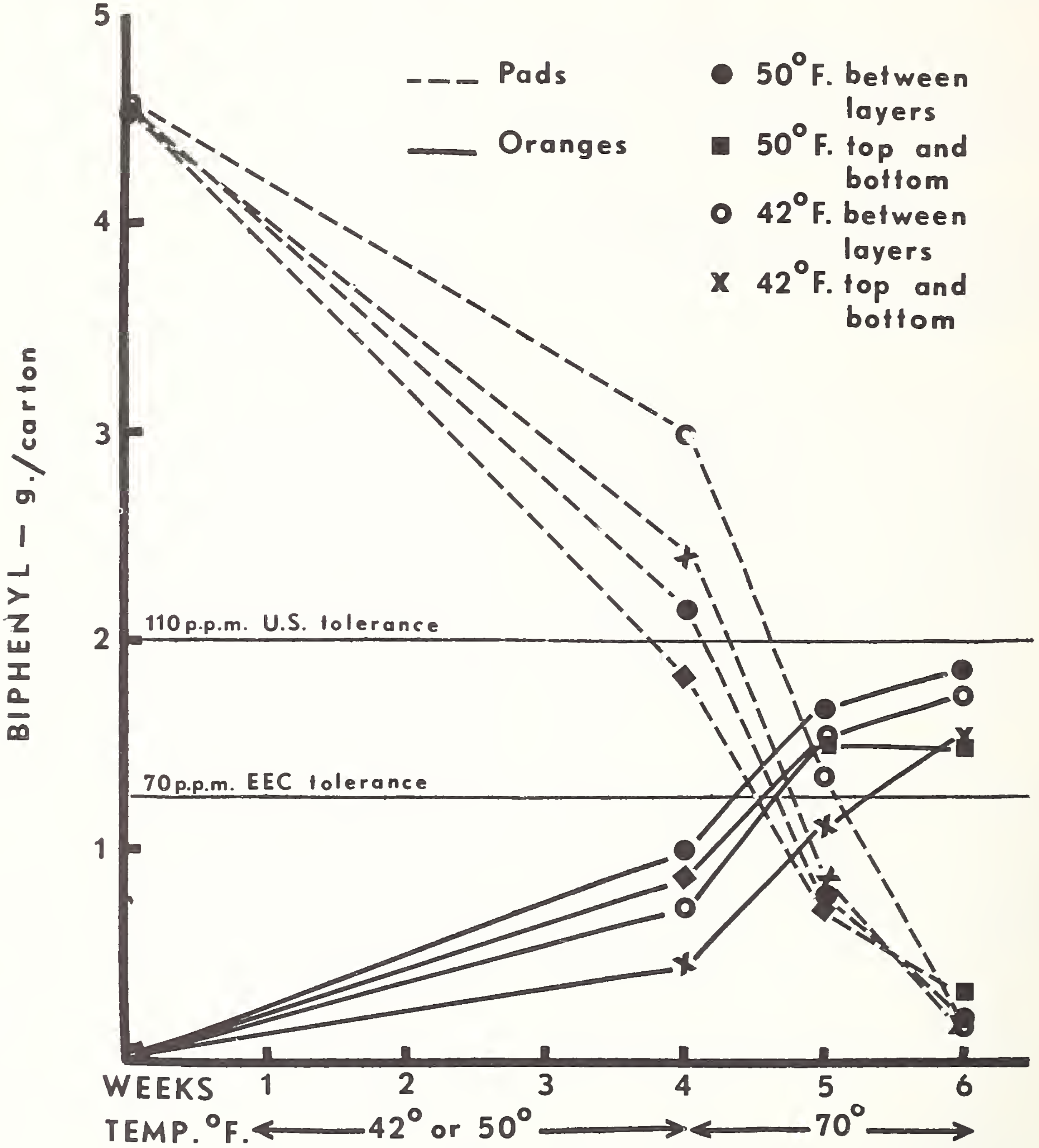

Figure 1.--Depletion of biphenyl from pads and biphenyl absorption by navel oranges when stored with pads between layers and at the top and bottom of the carton

70° with pads between layers was higher than that with pads at top and bottom, regardless of the initial 4-week storage temperature. At 6 weeks all residues exceeded the 70 p.p.m. EEC tolerance but were below the 110 p.p.m. U.S. tolerance. About 95 percent of the biphenyl was lost from the pads. After 4 weeks' storage at 50° plus 2 weeks at 70°, decay was 30 percent without biphenyl pads, 12 percent with pads between layers, and 19 percent with pads at top and bottom; after 4 weeks' storage at 42° plus 2 weeks at 70°, decay was 40, 22, and 28 percent, respectively. More decay at 42° than at 50° is not typical (6, pp. 12-14).

Average biphenyl residues from series B and C are shown in table 1. Three treatments

Table 1.--Biphenyl residues in pads per carton and in navel oranges after 2 and 4 weeks' storage at 50° F.

Treatment	Carton venting	Biphenyl content in--				
		Pads after--			Oranges after--	
		0 wk.	2 wk.	4 wk.	2 wk.	4 wk.
		Grams	Grams	Grams	P.p.m.	P.p.m.
2 pads, 2.32 g. biphenyl/pad						
Pads T & B[1]	Vented	4.67	2.97	1.47	35.2	60.9
Pads BTW[2,3]	Vented	4.64	2.86	1.56	44.1	68.8
2 pads, 1.40 g. biphenyl/pad						
Pads T & B[1]	Vented	2.71	1.21	.57	36.5	58.5
Pads T & B[1]	Nonvented	2.69	1.39	.75	41.9	62.3
Pads BTW[3]	Vented	2.80	1.14	.72	44.8	61.5
Pads BTW[3]	Nonvented	2.77	1.37	.89	50.6	72.5
3 pads, 1.07 g. biphenyl/pad						
Pads BTW[4]	Vented	3.22	1.36	.96	50.9	69.1
Pads BTW[4]	Nonvented	3.22	1.67	1.01	52.5	75.3
5 pads, 0.55 g. biphenyl/pad						
Pads BTW[5]	Vented	2.84	.53	.20	52.9	64.2
Pads BTW[5]	Nonvented	2.84	.90	.42	62.9	80.7
3 pads, 0.55 g. biphenyl/pad						
Pads BTW[4]	Vented	1.69	.32	.26	43.8	54.7
Pads BTW[4]	Nonvented	1.68	.48	.38	47.8	54.9
2 pads, 2.32 g. biphenyl/pad						
Pads T & B[1]						
Filler	Vented	4.63	2.78	1.86	36.4	55.7
No filler	Vented	4.67	2.97	1.47	35.2	60.9
1 pad, 2.41 g. biphenyl/pad						
Pad MID[6]						
Filler	Vented	2.42	1.47	1.01	39.5	52.4
No filler	Vented	2.41	1.57	1.14	40.3	55.3

[1] Pads at the top and bottom of the carton.
[2] Control.
[3] Pads between the first and second and the third and fourth layers of fruit.
[4] Pads between the second and third, the third and fourth, and the fourth and fifth layers of fruit.
[5] Pads under every layer of fruit.
[6] Pad between the third and fourth layers of fruit.

resulted in biphenyl levels in the fruit exceeding the 70 p.p.m. EEC tolerance but none exceeded the 110 p.p.m. U.S. tolerance. Biphenyl absorption was reduced 8 percent compared with the control, by placing one pad in the center of the carton. Oranges in nonvented cartons absorbed 13 percent more biphenyl than those stored in vented cartons. Oranges with two pads between layers absorbed 7 percent more biphenyl than those with pads at the top and bottom. Decay of the fruit ranged between 4 and 11 percent and was not related to the biphenyl treatments. The fruit was not inoculated.

Three treatments in series B were sampled weekly to facilitate plotting depletion of biphenyl from the pads and absorption of biphenyl by oranges (fig. 2). Biphenyl pads containing

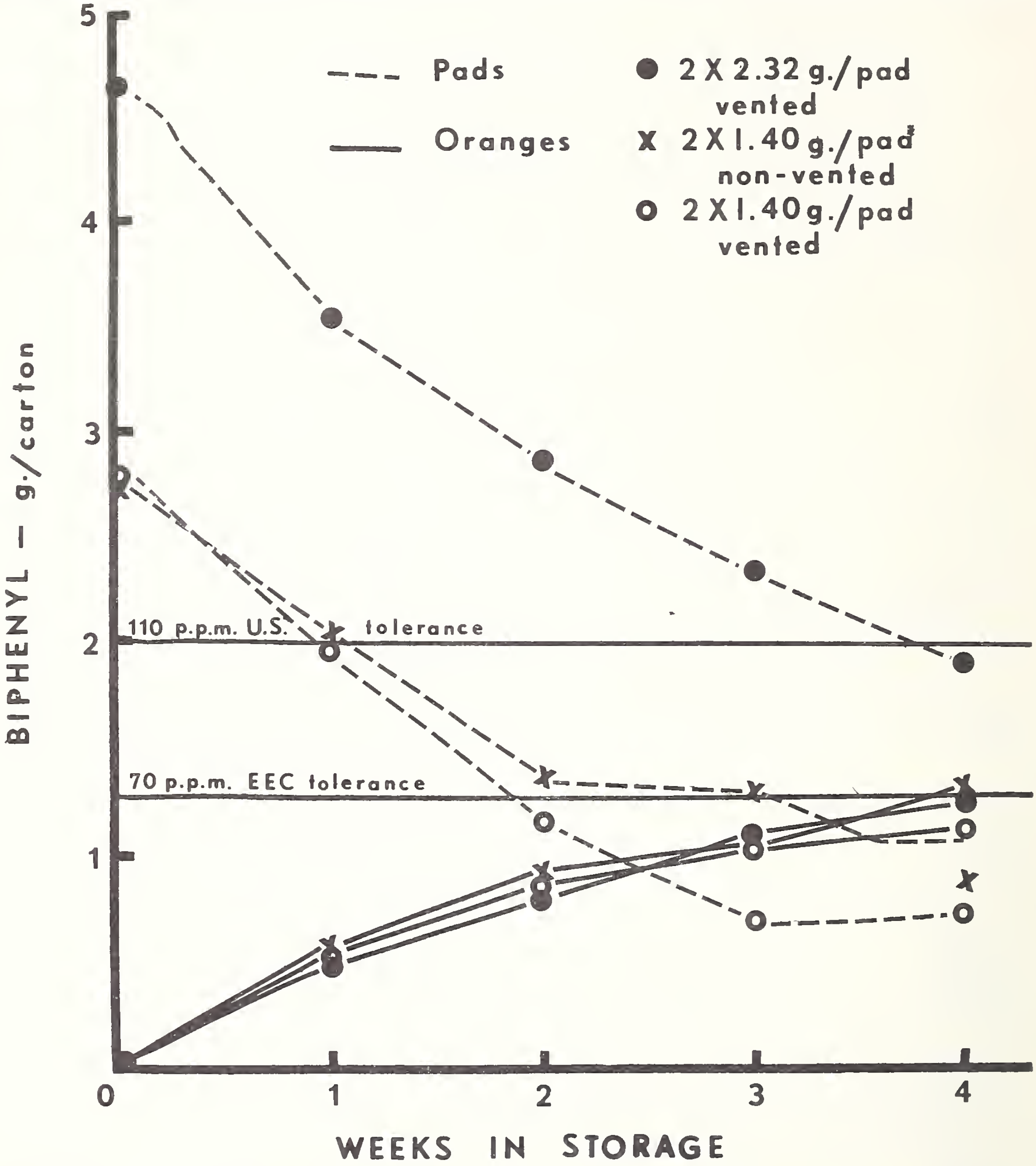

Figure 2.--Depletion of biphenyl from pads and biphenyl absorption by navel oranges when stored at 50° F. with biphenyl dosages of 4.64 and 2.80 g./carton.

2.32 g. lost 66 percent biphenyl and those containing 1.40 g. lost 75 percent in 4 weeks. Oranges absorbed 42 percent of the biphenyl lost from the pads containing 2.32 g. and 53 percent of that lost from the pads containing 1.40 g.

Biphenyl absorption by oranges increased as the number of sheets per carton increased regardless of the biphenyl dosage (fig. 3). The

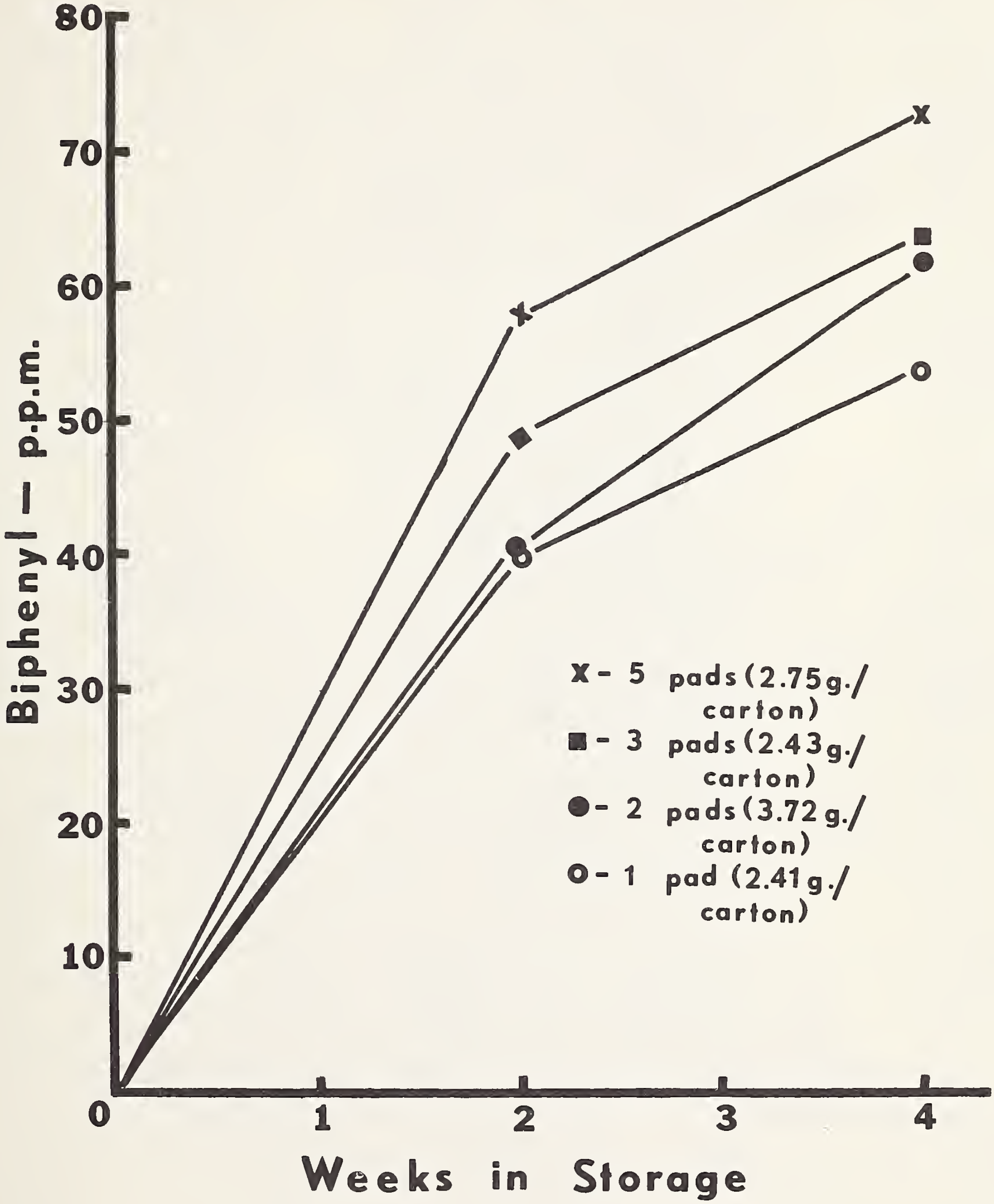

Figure 3.--Biphenyl absorption by navel oranges stored at 50° F. with 1,2,3, and 5 biphenyl pads per carton.

biphenyl dosages in the cartons containing one and five pads were 2.41 and 2.75 g., respectively; the dosages for two pads were 2.80 and 3.21 g.; and the dosages for three pads were 1.65 and 2.75 g. per carton. Five pads per carton lost 89 percent biphenyl whereas one pad per carton lost 57 percent. Oranges in cartons with five pads absorbed 52 percent of the biphenyl lost from the pads whereas oranges in cartons with one pad absorbed 69 percent of the biphenyl lost from the pad. Other tests have shown that the orange peel in direct contact with a biphenyl pad absorbed 55 percent more biphenyl than peel facing but not touching the pad. The orange half facing the biphenyl pad absorbed 29 percent more biphenyl than the half facing away from the biphenyl pad (data not shown).

Biphenyl residues from series D are shown in table 2. Waxed oranges absorbed more biphenyl than unwaxed oranges. Generally, biphenyl content increased with increasing coats of wax.

Table 2.--Biphenyl residues in oranges associated with different waxes and one, two, and three coats of wax

Wax no.	Numbers of coats of wax on oranges			
	0	1	2	3
	P.p.m.	P.p.m.	P.p.m.	P.p.m.
1	51.1	72.2	86.5	88.8
2	--	83.8	102.6	113.1
3	--	63.4	66.1	72.5
4	56.0	59.5	78.7	73.5
5	--	48.3	51.2	57.4
Average	53.5	65.5	77.0	81.0

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